Supporting Information for:

Synthesis of Polymer Dielectric Layers for Organic Thin Film Transistors via Surface-Initiated Ring-Opening Metathesis Polymerization

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Materials. Acetone, isopropyl alcohol, ethanol, 8-bromo-1-octene, tetrahydrofuran (anhydrous), hexamethyldisilathiane, tetrabutylammoniumfluoride (1.0 M in THF with 5% H_2O), and bicyclo[2.2.1]hept-2-ene (norbornene) were used as received from Aldrich. Dichloromethane (Aldrich, anhydrous) was degassed prior to use by sparging with argon. 1,2-dichloroethane (Aldrich, anhydrous) was first filtered through a plug of neutral alumina (Brockman Grade I – this procedure is necessary in order to have film growth), and then degassed by sparging with argon. 5-(Bicycloheptenyl)trichlorosilane (**3**) was purchased from Gelest, Inc., and used as received. Bicyclo[2.2.1]hept-5-ene-2-methanethiol (**4**) was prepared as described in the literature.[1] Catalysts **1**[2] and **2**[3] were prepared as described in the literature. 7-Octene-1-thiol (**5**) was prepared according to a literature procedure,[4] with 8-bromo-1-octene as starting material.

Substrate Preparation and Metal/Organic Semiconductor Deposition. Silicon wafers containing a 3000 Å, thermally grown oxide layer were obtained from Silicon Quest International. Gold substrates (typically composed of a 500 or 1000 Å layer of gold over a 50 or 100 Å layer of titanium, both vacuum deposited in an e-beam evaporator) were prepared on silicon wafers containing a native oxide layer (Silicon Quest International). Substrates were cut into 1 cm^2 squares, individually cleaned by sequential washings with acetone, deionized water, and iPrOH, and dried in a stream of dry nitrogen (N_2). The substrates were then soaked in a boiling solution of $H_2O/H_2O_2/NH_4OH$ (5:1:1) for 30 min, washed with water and iPrOH, and dried with dry N_2.

Surface Functionalization. In a typical procedure using gold substrates, self-assembled monolayers (SAMs) were formed by submerging freshly cleaned substrate squares in a filtered solution of thiol in absolute EtOH (typically 0.5 or 0.75 mM) for 24 h. The squares were then removed and washed, first with EtOH, then with iPrOH before being dried in a stream of dry N_2. Using Si/SiO_2 substrates, freshly cleaned squares were submerged for 6 h in a 0.5 wt% solution of trichlorosilane in pentane in a N_2 glovebox. The squares were then removed, sonicated for five min each in toluene (2 times), 50/50 toluene/acetone, and acetone, and dried in a stream of dry N_2.

Reaction of the olefin-functionalized substrates with catalyst was done in dichloromethane solutions of catalyst **1** or **2** (typically 13 or 25 mM) at room temperature (rt) or 40 °C. After the prescribed length of time, the squares were removed from solution, washed thoroughly with dichloromethane, and dried under N_2. They were then immediately placed in a fresh, filtered solution of norbornene in 1,2-dichloroethane and allowed to react for a prescribed length of time at rt or 40 °C. The squares were then washed thoroughly with dichloromethane and dried under vacuum.

Device Construction. For the FETs using a gold strip as the gate electrode deposited on SiO_2 (both lamination and direct deposition methods), linker **4** and catalyst **2** were used. Catalyst attachment and norbornene polymerization were done at rt for 10 min and 15 min, respectively. The thickness of the polynorbornene film was 1.2 μm for the lamination devices, and ranged from 800 to 1100 nm for the direct deposition samples. In mobility calculations, a width (W) of 2-3 mm and

length (L) of 1 mm were used for the laminated devices. A width of 940 μm and length of 240 μm were used for the direct deposition devices.

For the FETs using Si/SiO_2 as gate electrode, catalyst attachment was done with dichloromethane solutions of catalyst **1** or **2** at rt for 10 min, and the polymerizations were carried out with 1,2-dichloroethane solutions of norbornene (between 2 and 4 M) at rt, times varying between 15 and 40 min. The thickness of the polynorbornene films, which were very smooth and did not require annealing, ranged between 230 and 800 nm, but only those films thicker than 600 nm were used to make TFTs.

The organic semiconducting layer of pentacene (Aldrich) was deposited by thermal evaporation under vacuum (typically to a thickness of 300 Å). Gold overlayers were deposited in an e-beam evaporator under vacuum.

Characterization. Ellipsometric measurements were performed on a Rudolph Ellipsometer AutoEL. Profilometric measurements were measured using a Dektak 3030. Current-voltage characteristics were obtained with a Hewlett-Packard (HP) 4155A semiconductor parameter analyzer. AFM tapping mode data was acquired on a JEOL JSPM-4210 scanning probe microscope in an N_2 environment. "NONCONTACT ULTRASHARP" silicon cantilevers were purchased from NT-MDT, Ltd. Rutherford backscattering spectroscopy (RBS) and medium energy ion scattering (MEIS, a low energy ultrahigh resolution variant of RBS) were performed at the Rutgers University ion scattering facility. 1.5MeV He ions (in RBS) and 100keV protons (in MEIS) were used to quantify film composition and thickness.

References:

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